

REMOVAL OF ARSENIC FROM GROUNDWATER BY LIME SOFTENING WITH POWDERED COAL ADDITIVE

*A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY*

by
ABHIJIT DUTTA

to the
**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
APRIL, 1989**

dedicated to

my parents and Swapna

5-3 OCT 1989

CENTRAL LIBRARY
U.S. AIR FORCE

Acc. No. A. 105851

CE-1989-M-DUT-REM

T
628.114

3 08 11 11

CERTIFICATE

Certified that the work presented in this thesis entitled "Removal of Arsenic from Groundwater by Lime Softening with Powdered Coal Additive" by Abhijit Dutta has been carried out under my supervision and it has not been submitted elsewhere for a degree.

April, 1989



(Malay Chaudhuri)

Professor

Environmental Engineering Division
Department of Civil Engineering
Indian Institute of Technology
Kanpur

ACKNOWLEDGEMENTS

I wish to express my deep sense of gratitude and thankfulness to Dr. Malay Chaudhuri for his valuable counsel, patience, constant encouragement and alround assistance.

I take this opportunity to thank Dr.A.V.S.Prabhakara Rao, Dr. C. Venkobachar, Dr. Vinod Tare, Dr. D.K. Ghosh and Dr. (Mrs.) Leela Iyengar for their help and encouragement all throughout my stay at I.I.T., Kanpur.

I am extremely thankful to Sri R.C. Adhikari for his valuable and friendly advice and ready help throughout my work. My heartfelt thanks to Shri S.N. Mishra for his help in the laboratory.

I duly acknowledge the help received from Sri A.Hassan, Sri Nek Ram Sahu, Sri Vijay Bahadur and Sri Inderdev.

I am indehted to Sri J. Karthikeyan and my friend Soumyen Guha for their magnificent contribution in completion of my work.

I wish to extend my thanks to my all other friends, Vijay, Gopalkrishna, Rao, Chaurasia, Rajesh, Jawed, Parameshwar, Vinod and other intimate hallmates for their memorable company throughout my stay.

My thanks to Sri U.S. Misra for the care and pains taken for converting my scribbles into a legible form. Thanks are due to Sri V.P. Gupta for preparing the nice drawings for the thesis.

TABLE OF CONTENTS

1. INTRODUCTION	
2. PRESENT STATE OF KNOWLEDGE	
2.1 Arsenic: Its Occurrence and Effects	
2.1.1 Sources	
2.1.2 Levels in Water	
2.1.3 Health Effects	
2.2 Chemistry of Arsenic	
2.3 Removal of Arsenic from Water and Wastewater	1
2.4 Lime Softening/Precipitation and Arsenic Removal	1
3. SCOPE OF THE PRESENT STUDY	1
4. MATERIALS AND METHODS	1
4.1 Materials	1
4.1.1 Water	1
4.1.2 Coal	1
4.2 Methods	1
4.2.1 Arsenic Estimation	1
4.2.2 Lime Softening Test	2
4.2.3 Arsenic Removal by Calcium Carbonate and Magnesium Hydroxide	2
5. RESULTS AND DISCUSSION	24
5.1 Arsenic Removal from Arsenic Spiked IIT Kanpur Groundwater by Lime Softening	24
5.2 Arsenic Removal from Kachua Groundwater by Lime Softening	24
5.3 Arsenic Removal from Kachua Groundwater by Lime Softening with Powdered Coal Additive	27
5.4 Role of Calcium Carbonate and Magnesium Hydroxide in Arsenic Removal	29
6. SUMMARY AND RECOMMENDATIONS	32
REFERENCES	34

LIST OF TABLES

Number	Title	Page
1	Summary of Arsenic Treatment Methods and Removal Achieved	1
2	Precipitation Treatment of Arsenite and Arsenate in Gold Ore Extraction Wastewaters	11
3	Characteristics of Water Samples	18

LIST OF FIGURES

Number	Title	Page
1	Calibration curve for arsenic	21
2	Optimum mixing time for arsenic removal from arsenic spiked IIT Kanpur groundwater by lime softening	23
3	Arsenic removal from arsenic spiked IIT Kanpur groundwater by lime softening	25
4	Arsenic removal from Kachua groundwater by lime softening	25
5	Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater	26
6	Sorption of arsenic by powdered Giridih bituminous coal from Kachua groundwater	28
7	Optimum mixing time for arsenic removal from Kachua groundwater by lime softening with powdered Giridih bituminous coal additive	28
8	Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater with powdered Giridih bituminous coal additive (coal and lime added simultaneously)	30

LIST OF FIGURES

Number	Title	Page
9	Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater with powdered Giridih bituminous coal additive (coal and lime added separately)	30
10	Sorption of arsenic(III) by preformed calcium carbonate and magnesium hydroxide	31
11	Sorption of arsenic(V) by preformed calcium carbonate and magnesium hydroxide.	31

1. INTRODUCTION

The goal of the International Water Supply and Sanitation Decade (1981-90) is to provide safe and adequate drinking water to the entire world population. By no means, this is a challenging task and in the developing countries, the major obstacles in achieving this goal are the constraints of funds and skilled manpower. As an interim measure, most developing countries are resorting to groundwater supplies which are usually free from microbiological contaminants and may be supplied as drinking water without much treatment. However, in specific locations, groundwater supplies may be contaminated with toxic inorganic chemicals which may cause adverse health effects after prolonged exposure and efforts must be made to minimize them. On the basis of the health-related data concerning inorganic constituents, the World Health Organization (WHO) has recommended guideline values for nine of them which include arsenic (WHO, 1984a).

Arsenic is a ubiquitous element with metalloid properties. Its chemistry is complex and there are many different compounds of both inorganic and organic arsenic. In nature, it is widely distributed in a number of minerals, mainly as the arsenides of copper, nickel and iron or as arsenic sulfide or oxide. In water, arsenic is usually found in the form of arsenate (Pentavalent) or arsenite (trivalent); under reducing conditions, for instance, in deep-well waters, arsenite

predominates (WHO, 1981). Arsenic contamination of groundwater can result from leaching of man-made toxic arsenic compounds or from natural dissolution of minerals from the subterranean strata. High arsenic levels in groundwater were reported from many parts of the world which include Taiwan (Kuo, 1968; Shen, 1973), Japan (Terada, 1960), Argentina (Arguello et al., 1938) and USA (Goldblatt et al., 1963).

In India, the first case of arsenic poisoning was reported from a few villages in the northern parts of the country (Datta and Kaul, 1976). With recent reports of arsenical dermatosis in 14 villages in 5 districts of West Bengal, the problem has assumed significance. High levels of arsenic in the tubewell water in these areas of West Bengal were linked to arsenical dermatosis and skin cancer (Chakraborty and Saha, 1987). Upto August 1986, 197 cases of arsenical dermatosis were reported and diffuse melanosis was found in all the patients with 34.5% showing liver enlargement. At present, the figure is presumably more than 1000. The mean arsenic level in 31 water samples collected from the affected areas was reported to be 0.64 mg/L.

Conventional water treatment involving ferrous sulfate coagulation followed by settling and filtration yields significant arsenic removal (Buswell et al., 1943). According to Shen (1973), a full-scale water treatment plant involving chlorine oxidation followed by ferric chloride coagulation

and sand filtration produced arsenic-free water from arsenic contaminated (0.06 - 2.0 mg/L) well water. In a recent field study (Fox, 1989), sorption on activated alumina, ion-exchange and reverse osmosis were observed to be effective in point-of-use treatment devices in removing arsenic from ground water. However, these methods of arsenic removal do not appear to be feasible in terms of village-level application, primarily due to high cost and skilled operation.

The present study was undertaken with a view to provide a low-cost solution to the drinking water arsenic problem which would be feasible in terms of village-level application. Removal of arsenic by lime softening from tubewell water samples collected from one of the affected areas of West Bengal was studied in the laboratory along with powdered coal additive for possible enhancement of removal and reduction of lime dose.

2. PRESENT STATE OF KNOWLEDGE

2.1 Arsenic : Its Occurrence and Effects

2.1.1 Sources

Arsenic occurs ubiquitously in nature and is usually present in the form of compounds with sulfur and with many metals (copper, cobalt, iron, lead, zinc, etc); the average concentration in the earth's crust is about 2 mg/kg (WHO, 1984b). In the oceans, the arsenic concentration is approximately 14 tons/cu mi in many areas (Wenk, 1969). Although arsenic exists in various valency states and in both organic and inorganic forms, the levels of environmental arsenic are normally reported in terms of total arsenic.

Common mineral forms of arsenic compounds are arsenopyrite ($\text{FeS}_2 \cdot \text{FeAs}_2$), realgar (AsS), and orpiment (As_2S_3) (Hurlbut, 1968). Methylated arsenic compounds occur due to biological activities. In seawater, some marine organisms transform inorganic arsenic into more complex organic compounds like arsenobetaine, arsenochlorine, and arsoniumphospholipids (WHO, 1981). In air, urban areas and particularly industrial towns, levels of arsenic have exceeded $1 \mu\text{g}/\text{m}^3$ (WHO, 1984b). Arsenic is also present in most foodstuffs. The average dietary sources of arsenic seem to give rise to an intake of about $30 \mu\text{g}/\text{kg}$ of body weight per day (WHO, 1984b). In some localized geographic areas, commercial use and production of arsenic compounds have resulted in significant elevation in

the amount of environmental arsenic above natural background levels. Arsenic compounds are mainly used in agriculture and forestry as pesticides, herbicides and silvicides. Arsenic trioxide, lead arsenate and calcium arsenate are used as insecticides and are highly toxic (Gulledge and O'Connor, 1973; Woodward, 1960).

2.1.2 Levels in Water

Many arsenic compounds are water-soluble and, thus, contamination of water can occur (WHO, 1984b). Arsenic is mainly transported in the environment by water. In spite of its ubiquitousness in nature, most of the arsenic found in water, except those occurring naturally, derived from industrial discharges. Gold mining activities, arsenic sulfide factory, coal preparation waste and fly ash from coal fired plants result in the contamination of water (WHO, 1981).

A large number of water supplies contain very low arsenic levels i.e., well below 0.01 mg/L (WHO, 1984b). In special situations, gross contamination of well supplies has occurred and several milligrams of arsenic per litre of water have resulted (National Research Council, 1977). High arsenic levels in groundwaters have been reported from many parts of the world, e.g., 0.6-2.0 mg/L in Taiwan (Kuo, 1968; Shen 1973), 3.0 mg/L in Japan (Terada, 1960), 0.9-3.4 mg/L in Argentina (Arguello et al., 1938) and 0.07-1.7 mg/L in USA (Goldblatt et al., 1963). In India, Datta and Kaul (1976) found 29.4% of water samples from wells, 50% from tubewells and 35.7% from springs in and around Chandigarh to contain

high levels of arsenic. Chakraborty and Saha (1987) reported 0.64 mg/L mean arsenic level in tubewell (110-150 feet deep) water samples collected from several districts of West Bengal, the range being 0.2-2.0 mg/L.

2.1.3 Health Effects

The toxicity of arsenic compounds depends on the chemical and physical form of the compound, the route by which it enters the body, the dose and duration of exposure, dietary levels of interacting elements, and the age and sex of the exposed individual. Inorganic arsenic is more toxic than organic arsenic; trivalent inorganic arsenic is more hazardous than the pentavalent form. It is recommended that, when water is found to contain arsenic at levels of 0.05 mg/L, an attempt should be made to ascertain the valency and chemical forms of the element (WHO, 1984b).

Arsenical poisoning can affect the gastrointestinal tract, nervous system, the respiratory tract, and the skin (Quebec Ministry of Supply and Services, 1979). Chronic poisoning is manifested by general muscular weakness, headache, numbness, stiffness, crawling and prickling sensations in the toes, feet and legs, loss of appetite and nausea, vomiting of blood-stained or bile-stained mucus and constipation, inflammation of the mucous membranes in the eye, nose and larynx, loss of nails and hairs, skin lesions, etc. (Gulledge and O'Connor, 1973; Quebec Ministry of Supply and Services, 1979).

Chen and Wu (1962) reported high incidence of hyperkeratosis and skin cancer in Taiwan after consumption of water containing more than 0.3 mg/L arsenic. Tseng et al. (1961) also observed association of skin cancer with drinking wellwater containing 0.5 mg/L arsenic. According to Rosenberg (1973), 0.6 mg/L arsenic was perhaps responsible for arsenic poisoning in children in Chile. Applying the linear non-threshold model, a WHO Task Group estimated that a life-time exposure to arsenic in drinking water at a concentration of 0.2 mg/L gave a 5% risk of getting cancer of the skin (WHO, 1984b). Chakraborty and Saha (1987) also observed that presence of arsenic levels less than 0.2 mg/L did not produce arsenicism; however, arsenical dermatosis was reported in 14 villages in 5 districts of West Bengal having arsenic levels in the tubewell water in the range 0.2-2.0 mg/L. Dermatological manifestations of arsenicism were also reported from Chile (Borgono and Greiber, 1972).

Based on human health data, a 0.05 mg/L level of arsenic in drinking water is not associated with any adverse health effects. Estimates have been made of the risk of cancer from low intakes of arsenic, but these are very uncertain. At an arsenic level of 0.05 mg/L the contribution made by water to the total intake will normally be about one-half to two-thirds; for very low dietary intakes of arsenic, the proportion provided by water may be somewhat higher. Arsenic in drinking-water will normally be the main source of inorganic arsenic. An arsenic concentration of 0.05 mg/L has been recommended as

a guideline value for drinking water (WHO, 1984a).

2.2 Chemistry of Arsenic

Arsenic (atomic weight = 74.9216) is a shiny, gray, brittle element possessing both metallic and non-metallic properties (Train, 1979). Arsenic exists in the trivalent and pentavalent states and its compounds may be either organic or inorganic. Among inorganic compounds, arsenic trioxide or arsenous oxide (As_2O_3 or As_4O_6), arsenic pentoxide (As_2O_5), arsenous acid (H_3AsO_3), arsenious acid (HAsO_2), arsenites (salts of arsenous acid) (H_2AsO_3^- , HASO_3^{2-} or AsO_3^{3-}), arsenates (salts of arsenious acid) (AsO_2^-), arsenic acid (H_3AsO_4), arsenates (salts of arsenic acid) (H_2AsO_4^- , HASO_4^{2-} or AsO_4^{3-}), arsenic sulfide (As_2S_3) are important (WHO, 1981).

Some properties of arsenical compounds are (a) arsenic trioxide (As_2O_3) is most important, more toxic than pentavalent arsenic, sparingly soluble in water (2% at 25°C), highly soluble in either HCl or in alkali, and in the form of arsenite in aqueous solution; (b) alkali earth metals (like Na, K) combine with arsenite or arsanate anions to form highly soluble salts; (c) arsanates and arsenic acid are strong oxidants and oxidize I^- to I_3^- ; (d) under air saturated oxidizing condition As(V) predominates; (e) arsenic forms precipitates with phosphates; and (f) leaching of arsenate in soil is slow because of binding to hydrous oxides of iron and aluminium (WHO, 1981).

Sodium arsenite (NaAsO_2) is the most frequently used form of arsenic. When sodium arsenite is added to water with a pH less than 9.5, the predominant aqueous form is HAsO_2 . If the solution pH is greater than 9.5, AsO_2^- is the predominant species. Arsenite, As(III), is oxidized to arsenate, As(V) in the presence of oxygen, chlorine, or potassium permanganate (Gulledge and O'Connor, 1973).

The other species of arsenic that is commonly found in water is the arsenate ion (AsO_4^{3-}), which is not so toxic, as arsanite (Gulledge and O'Connor, 1973). In a system including oxygen and sulfur, Ferguson and Gavis (1972) showed that the soluble arsenite species are H_3AsO_3 , H_2AsO_3^- , and HAsO_3^{2-} . The soluble arsanate species are H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . In the pH range 4-10, the predominant arsenite form is H_3AsO_3 and the predominant arsanate species are H_2AsO_4^- and HAsO_4^{2-} . The rate of oxidation of arsenic(III) to arsenic(V) with oxygen was found to be very slow at natural pH values, but proceeds measurably in several days in strong alkaline or acid solutions (Ferguson and Gavis, 1972).

Sorg and Logsdon (1978) reported that based upon a general review of the literature, arsenite is more likely to be found in anaerobic groundwaters and arsanate in aerobic surface waters. Because information on conventional coagulation and lime softening treatment shows that arsenic removal is valence dependent, steps should be taken to identify the arsenic form causing an arsenic problem before evaluating possible solutions.

2.3 Removal of Arsenic from Water and Wastewater

The oxidation state of the aqueous form appears to have a significant effect upon treatment efficiency for arsenic removal. More up-to-date information is available on the removal of arsenic(V) from drinking water. In comparison information on the removal of arsenic(III) or total arsenic from drinking water is scanty.

Major treatment methods for arsenic removal include sulfide precipitation or complexation with polyvalent heavy metals such as ferric ion and coprecipitation with the metal hydroxide, plus adsorption into the coagulant floc, with enmeshment of particulate arsenic. Other processes used, with varying degree of success include adsorption into activated carbon and alumina, and ion-exchange (Patterson, 1975).

A summary of the treatment methods and the arsenic removal efficiencies for industrial wastewater treatment is given in Tables 1 and 2 (Patterson, 1975; Rosehart and Lee, 1972). It has been reported that effluent arsenic levels of 0.05 mg/L are obtainable by precipitation of arsenic as the sulfide, with addition of sodium or hydrogen sulfide at pH 6-7 (Curry, 1972). Sulfide precipitation has been found effective for arsenate, but ineffective for arsenite; ferrous sulfate precipitation is also active in removing arsenic(V) only, whereas, lime is effective on both arsenite and arsenate waste streams, since arsenite converts to the pentavalent form at high pH (Rosehart and Lee, 1972).

Table 1. Summary of Arsenic Treatment Methods and Removals Achieved

Treatment	Initial Arsenic (mg/L)	Final Arsenic (mg/L)	Removal (%)
Charcoal Filtration	0.2	0.06	70
Lime Softening	0.2	0.03	85
Lime Softening	0.5	0.03	95
Precipitation with Lime plus Iron	---	0.05	--
Precipitation with Alum	0.35	0.003-0.005	85-92
Precipitation with Ferric Sulfate	0.31-0.35	0.003-0.006	98-99
Precipitation with Ferric Sulfate	25.0	5	80
Precipitation with Ferric Chloride	3.0	0.05	98
Precipitation with Ferric Chloride	0.58-0.90	0.0-0.13	81-100
Precipitation with Ferric Hydroxide	---	0.6	--
Precipitation with Ferric Hydroxide	362.0	15-20	94-96
Ferric Sulfide Filter Bed	0.8	0.05	94
Precipitation with Sulfide	---	0.05	--
Precipitation with Sulfide	132.0	26.4	80

Adapted from Patterson (1975).

Table 2. Precipitation Treatment of Arsenite and Arsenate in Gold Ore Extraction Wastewaters

Precipitation Chemical	Arsenic Form	Optimal pH	Removal (%)	Optimal Ratio of Precipitation Ion and Arsenic Ion
Ferrous Sulfate	AsO_4^{-3}	8	94	$\frac{\text{Fe}^{+2}}{\text{As}} = 1.5$
	AsO_2^-	No Precipitation	0	
Ferric Chloride	AsO_4^{-3}	9	90	$\frac{\text{Fe}^{+3}}{\text{As}} = 4.0$
	AsO_2^-	8	95	
Alum	AsO_4^{-3}	7-8	90	$\frac{\text{Al}^{+3}}{\text{As}} = 4.0$
	AsO_2^-	7-8	95	
Sodium Sulfide	AsO_4^{-3}	7	80	$\frac{\text{S}^{=}}{\text{As}} = 0.5$
	AsO_2^-	No Precipitation	0	
Lime	AsO_4^{-3}	12	95	$\frac{\text{Ca}^{+2}}{\text{As}} = 9.8$
	AsO_2^-	12	95	
Caustic	AsO_4^{-3}	10	80	$\frac{\text{Na}^{+2}}{\text{As}} = 3.8$
	AsO_2^-	No Precipitation	0	

Adapted from Rosehart and Lee (1972).

Conventional water treatment involving ferric sulfate coagulation followed by settling and filtration yields significant arsenic removal (Buswell et al., 1942; Gullledge and O'Connor, 1975). Gullledge and O'Connor (1975) reported maximum of 93.6% and 99.9% removal of As(V) by adsorption on hydrous aluminium oxide and hydrous ferric oxide, respectively. Ferrous, ferric and alum coagulant treatments of arsenic-contaminated water have also been reported by others

(Trelles and Amato, 1950; Berezman, 1956; Shen, 1973).

The mechanism of coprecipitation is the probable explanation for soluble arsenic removals reported by all coagulation processes. Stable complexes of arsenate and arsenite form with most polyvalent metals, particularly iron, aluminium and zinc, and these complexes are captured by the hydroxide precipitation of these metals at the pH of metal hydroxide formation (Patterson, 1975).

Chemical oxidation of arsenite to arsenate by chlorine or potassium permanganate, prior to coagulation treatment, improves arsenic removal indicates that arsenate forms the more stable complex with the precipitating metal (Shen, 1973).

Shen (1973) also reported that plain sedimentation had some effect on the removal of arsenic from water (48.7% removal after 15d quiescent settling). He also studied removal using special ion-exchanger and concluded that removal of arsenic from natural water was well but was too costly and complex. Sand and anthracite filtration showed good removal (from an initial concentration of 1.0 mg/L to effluent concentrations of 0.03 mg/L for sand and 0.01 mg/L for anthracite); slow sand filtration gave better results than rapid filtration (Shen, 1973).

Treatment using alumina with proper pH adjustment and treatment using charcoal are also feasible removal techniques for arsenic (Bellack, 1971; Hathway and Rubel, 1987). Removal of As(V) from water by activated carbon was tested by Huang

and Fu (1984) who reported 61% removal by D-X type granular activated carbon and 84% removal by D-XI type powdered activated carbon, and maximum As(V) removal occurred at pH 4 to 5. In a recent field study (Fox, 1989), sorption on activated alumina, ion-exchange and reverse osmosis were observed to be effective in point-of-use treatment devices in removing arsenic from groundwater.

2.4 Lime Softening/Precipitation and Arsenic Removal

In lime softening process, an appropriate amount of hydrated lime, Ca(OH)_2 , is added to soften a hard water. Calcium carbonate is a major component of the precipitate and if magnesium content as well as pH is sufficiently high (pH 10), magnesium hydroxide is also formed. Lime precipitation is also extensively used in the treatment of industrial wastewater to remove metals as precipitates by raising the pH with lime; precipitation of magnesium results in increased removal efficiency due to absorption of metal complexes onto magnesium hydroxide flocs. A status review by Bhatla et al. (1980) indicates that priority inorganic pollutants like arsenic, cadmium, chromium (trivalent), copper, lead, nickel, silver and zinc can be effectively removed by lime precipitation.

The literature information related to removal of arsenic from groundwater by lime softening is rather scanty. Trelles and Amato (1950) reported removal of arsenic from hard turbid water by lime. According to Sorg and Logsdon (1978),

arsenic can be removed effectively from hard water by lime softening, with the amount of removal dependent on the pH and the valency of arsenic. Laboratory study by Logsdon et al. (1974) showed that arsenic(V) was more readily removed from hard water than arsenic(III) and that removals of both forms increased with increasing pH. At pH 10.5 and above, almost 100% removal was obtained on hard water ($300 \text{ mg CaCO}_3/\text{L}$) spiked with 0.4 mg/L arsenic(V). The best removal of arsenic(III) was about 80% at pH 11.1 and above. Below the optimum pH range, both arsenic(V) and arsenic(III) removals decreased with decreasing pH, with arsenic(V) removals always higher than arsenic(III) removals.

Laguitton (1976) observed lime precipitation to be the most economic treatment for gold-mine arsenical slurries when pH was raised to above 12. According to Patterson (1975), an effluent arsenic level of 0.03 mg/L can be achieved by lime precipitation from initial arsenic concentration of $0.2\text{--}0.5 \text{ mg/L}$. Sedova et al. (1974) reported $0.006\text{--}0.10 \text{ mg/L}$ effluent arsenic concentration by lime precipitation of wastewater containing $60\text{--}2400 \text{ mg/L}$ arsenic. Lyubman et al (1981) reported a study on arsenic removal from sulfuric acid and arsenic(III) containing wastewater by lime precipitation.

3. SCOPE OF THE PRESENT STUDY

In specific locations, groundwater supplies contaminated with arsenic may pose a rather serious problem as arsenic causes adverse health effects after prolonged exposure. The situation prevailing in the rural areas of five districts of West Bengal is an ample example of such a situation. Effective methods of arsenic removal from groundwater include conventional water treatment involving coagulation followed by settling and filtration as well as point-of-use devices employing ion-exchange, reverse osmosis and activated alumina. However, these methods do not appear to be feasible in terms of village-level application in a developing country, primarily due to skilled operation and high cost. Hence, efforts should be made to investigate the potential of low-cost, easy-to-operate treatment methods in removing arsenic from groundwater. In view of the reported effectiveness of lime softening in removing arsenic(III) from spiked groundwater (Logsdon et al., 1974), removal of arsenic by lime softening from tubewell water samples collected from one of the affected areas of West Bengal was studied in the laboratory along with powdered coal (Giridih bituminous coal) additive for possible enhancement of removal. The study was conducted in the laboratory along the following lines.

a. Analysis of tubewell water samples collected from Kachua village, 24 Paraganas (N), West Bengal in terms of

arsenic content as well as arsenic forms (trivalent or pentavalent).

b. Experiments, using arsenic spiked IIT Kanpur groundwater, to standardize a low-volume procedure for lime softening test.

c. Lime softening test with arsenic spiked IIT Kanpur groundwater and Kachua groundwater.

d. Lime softening test with Kachua groundwater with powdered coal additive for possible enhancement of arsenic removal and reduction of lime dose.

e. Relative role of the lime softening precipitates, e.g., calcium carbonate and magnesium hydroxide in arsenic removal.

4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Water

IIT Kanpur groundwater, collected from tubewell No. 3, spiked with arsenic(III) (sodium arsenite, NaAsO_2), was used to standardize a procedure for lime softening test. Groundwater samples collected from a household tubewell in Kachua village, 24 Parganas (N), West Bengal was used in the lime softening tests. The Kachua groundwater was analysed in terms of arsenic content as well as arsenic forms (trivalent or pentavalent). The water characteristics are presented in Table 3.

Table 3. Characteristics of Water Samples

Parameter	IIT Kanpur Ground- water	Kachua Groundwater	
		Sample 1	Sample 2
pH	8.4	7.9	8.1
Alkalinity, mg/L as CaCO_3	515	490	500
Hardness, mg/L as CaCO_3	160	385	367
Calcium, mg/L as CaCO_3	63	290	278
Magnesium, mg/L as CaCO_3	97	95	89
Conductivity, $\mu\text{mhos/cm}$	5.5×10^{-4} at 22°C	6.7×10^{-4} at 20°C	6.0×10^{-4} at 20°C
Total arsenic, mg/L	Not detected	0.45-0.47	0.68-0.70
Arsenic(III), mg/L	--	--	0.59-0.60

4.1.2 Coal

Powdered Giridih bituminous coal passing through 75 μm sieve, was used in lime softening tests with powdered coal additive. The coal was initially ground to 600 μm , washed with distilled water to remove any adhered impurities, dried at 103°C and subsequently pulverised and sieved through a 75 μm sieve.

4.2 Methods

4.2.1 Arsenic Estimation

Arsenic was estimated by the silver diethyldithiocarbamate (SDDC) method (Standard Methods, 1985). In the method, inorganic arsenic is reduced to arsine (AsH_3) by zinc in acidic (HCl) environment in a Gutzeit generator which is absorbed by SDDC dissolved in pyridine to produce a soluble red complex suitable for photometric measurement.

In the procedure, a 35 mL sample or a suitable aliquot was taken in a clean generator bottle to which 5 mL concentrated HCl , 2 mL KI solution (15g of KI in 100 mL distilled water, stored in a brown bottle), and 0.4 mL SnCl_2 reagent (40 g of arsenic free $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL conc. HCl) were added successively with thorough mixing after each addition. 15 min were allowed for reduction of arsenic to the tri-valent state. When only arsenic(III) was determined KI and SnCl_2 were not added. Glass wool impregnated with lead acetate solution (10 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 100 mL distilled

water) was placed in the scrubber and 3 mL of SDDC reagent (1.25 g of silver diethyldithiocarbamate, $\text{AgSCSN}(\text{C}_2\text{H}_5)$, in 250 mL pyridine, $\text{C}_5\text{H}_5\text{N}$) was injected into the absorber tube. About 3g zinc (granulated) metal was added to the generator and the scrubber-absorber assembly was connected air tight immediately. The generator was then warmed slightly and kept for 1h for complete evolution of arsenic. Thereafter, the solution from the absorber was poured directly into 1 cm cell and the absorbance was measured at 535 nm.

Standard arsenic solution (1000 mg/L) was prepared by dissolving 1.73g sodium arsenite (NaAsO_2) in 1000 mL distilled water. The standard curve for arsenic determination was prepared with 0, 1, 2, 5 and 10 μg arsenic and is shown in Fig. 1. Minimum detectable concentration by this method is 1 μg of arsenic.

4.2.2 Lime Softening Test

Background lime softening experiments, using arsenic(III) (sodium arsenite, NaAsO_2) spiked IIT Kanpur groundwater, were conducted to standardize a procedure for low-volume batch lime softening test for use with the Kachua groundwater. It may be pointed out here that arsenic exists predominantly in arsenic(III) form in groundwater and it is further supported by the characteristics of the Kachua groundwater (Table 3). In the procedure, 75 mL arsenic(III) (1.0 mg/L) spiked groundwater in 100 mL plastic bottles with 2000 mg/L lime ($\text{Ca}(\text{OH})_2$) were agitated in an end-over-end

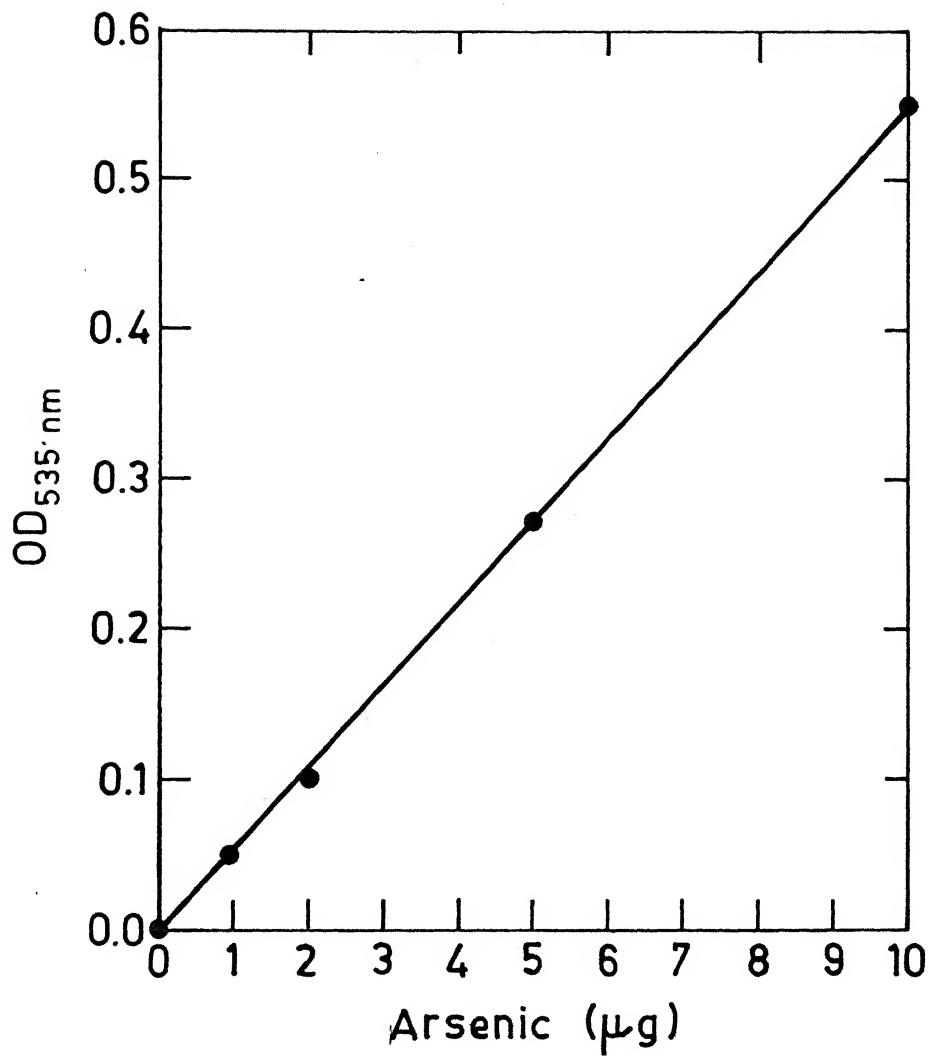


Fig. 1. Calibration curve for arsenic.

shaker at 20 rpm for 5, 10, 20, 30, 40, 50, 60, 70 and 90 min. Following agitation, the contents were filtered through Whatman No. 42 filter paper using a vacuum filter assembly. An initial filtrate volume of 15 mL was discarded and the remaining was immediately analysed for pH, arsenic and turbidity. Figure 2 shows the effect of mixing time on arsenic removal. Also, no turbidity was detected in the filtrates. Based on the results, this low-volume lime softening test procedure, employing 45 min mixing time and filtration through Whatman No. 42 filter paper, was used as a standard procedure.

4.2.3 Arsenic Removal by Calcium Carbonate and Magnesium Hydroxide

To study the relative role of the lime softening precipitates in arsenic removal, separate experiments were conducted with preformed calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) precipitates and 1.0 mg/L arsenic(III) (sodium arsenite, NaAsO_2) or arsenic(V) (sodium arsenate, Na_3AsO_4) solution in triple distilled water. Calcium carbonate and magnesium hydroxide precipitates were prepared by reacting stoichiometric quantities of calcium hydroxide and sodium carbonate, and magnesium chloride and sodium hydroxide, respectively. The precipitates were washed several times with triple distilled water and analysed for suspended solids concentration. Using a procedure similar to the lime softening test, arsenic(III) and arsenic(V) sorption by various dosages of the precipitates was evaluated.

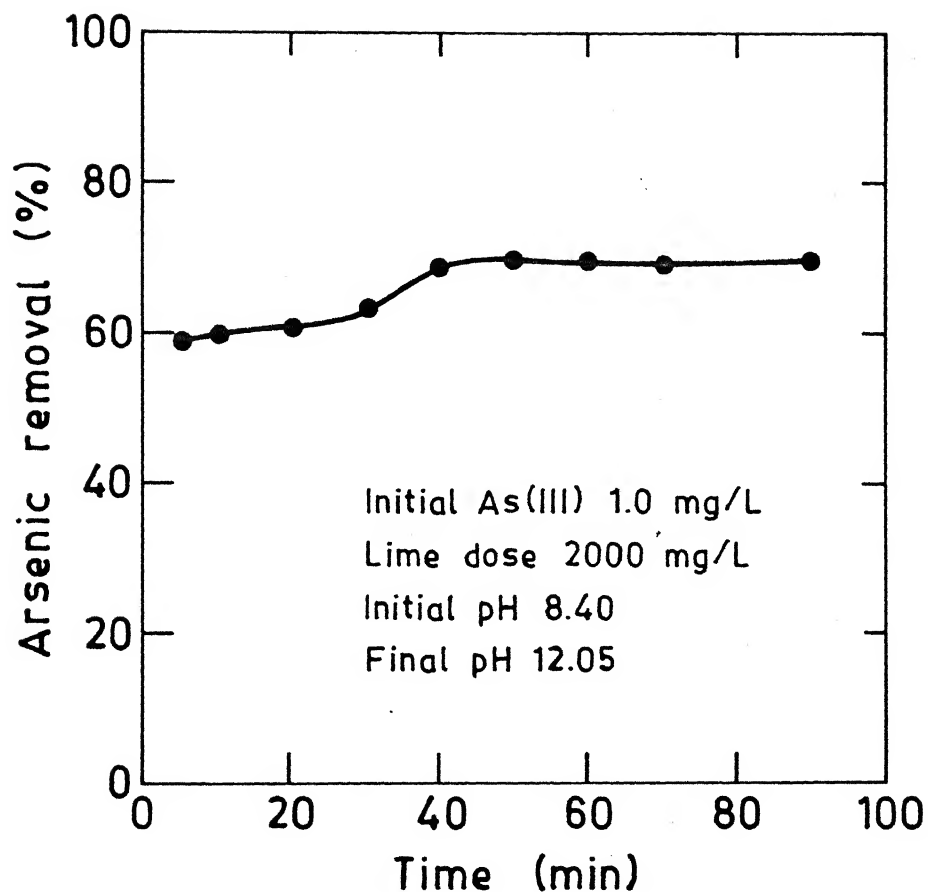


Fig. 2. Optimum mixing time for arsenic removal from arsenic spiked IIT Kanpur groundwater by lime softening.

5. RESULTS AND DISCUSSION

Results of all experiments are presented in graphical form followed by a discussion of each phase of the experimental work. All experiments were performed in duplicate or triplicate and the typical results, using mean of the experimental values, are reported.

5.1 Arsenic Removal from Arsenic Spiked IIT Kanpur Groundwater by Lime Softening

Lime softening tests, using arsenic(III) spiked (1.0 and 2.0 mg/L) IIT Kanpur groundwater, were conducted to study the effect of lime dose vis-a-vis pH on arsenic removal and to provide a background for the lime softening test with the Kachua groundwater. The results presented in Fig. 3 show that an arsenic removal of 77% can be achieved with a lime dose of 1250 mg/L (pH 11.75). Logsdon et al. (1974) reported similar removal at pH 11.0 from 0.4 mg/L arsenic(III) spiked groundwater. Also, the effect of initial arsenic(III) concentration on removal observed is similar to that reported by Logsdon et al. (1974).

5.2 Arsenic Removal from Kachua Groundwater by Lime Softening

Figure 4 shows the results of the lime softening test with Kachua groundwater which indicate an arsenic removal of 89% at a lime dose of 1250 mg/L (pH 11.80). However, the residual arsenic concentration (0.07 mg/L) is above the WHO guideline value of 0.05 mg/L (Fig. 5).

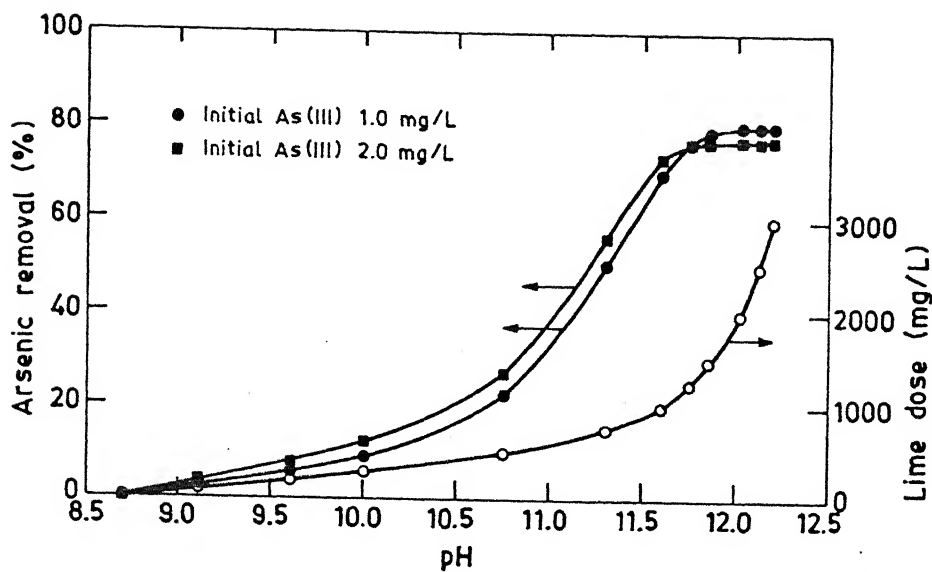


Fig. 3. Arsenic removal from arsenic spiked IIT Kanpur groundwater by lime softening.

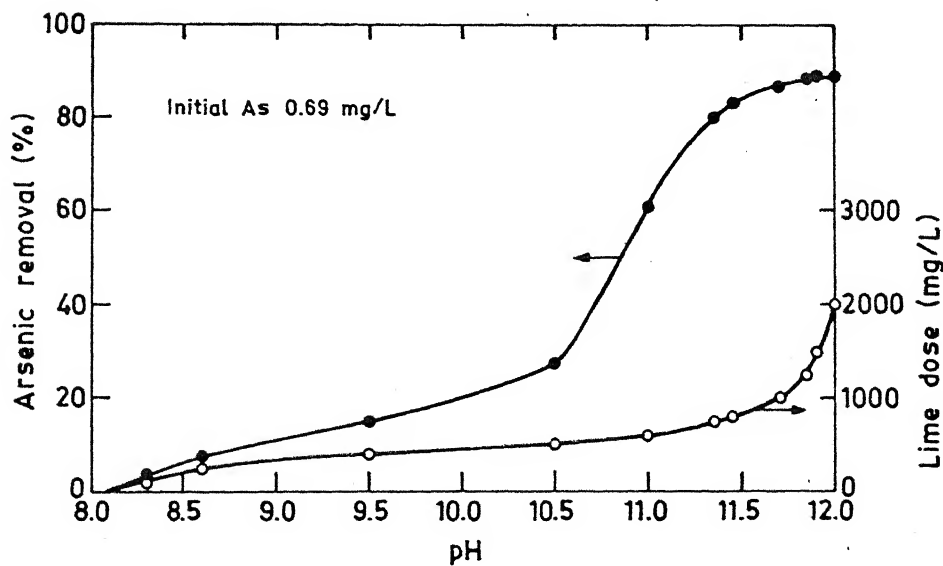


Fig. 4. Arsenic removal from Kachua groundwater by lime softening.

CENTRAL LIBRARY
IIT KANPUR
103851

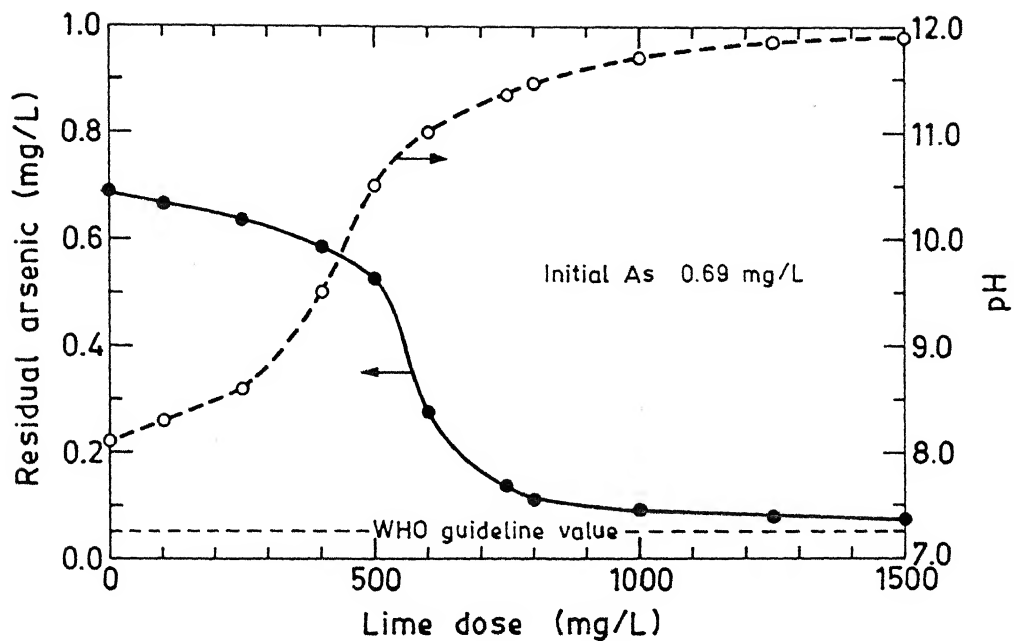


Fig. 5. Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater.

In the lime softening study of Logsdon et al. (1974), best removals of arsenic(III) did not exceed 80%; however, in contrast, removals of arsenic(V) and arsenic(III) following chlorination (to convert arsenic(III) to arsenic(V)) were 90% or higher for initial arsenic concentration of 0.1-10.0 mg/L. Conceivably, oxidation by chlorination or potassium permanganate addition may lead to higher arsenic removal from the Kachua groundwater. In view of the cost and operational difficulties of using chlorine or potassium permanganate and ability of coal to remove heavy metals in general (Cullen and Siviour, 1982) and arsenic in particular (Guha, 1989), it was thought appropriate to investigate possible enhancement of arsenic removal by lime softening with powdered coal additive.

5.3 Arsenic Removal from Kachua Groundwater by Lime Softening with Powdered Coal Additive

Preliminary experiments were conducted to study arsenic sorption by powdered Giridih bituminous coal, using both arsenic(III) spiked IIT Kanpur groundwater and Kachua groundwater, to provide the necessary background for the lime softening test with powdered coal additive. In a kinetic study (75 mL arsenic(III) spiked (1.0 mg/L) IIT Kanpur groundwater; coal 5g/L; pH 8.4), a contact time of 1h was found to produce 22-23% arsenic sorption and there was no further increase in sorption beyond 1h. Effect of coal dose on arsenic sorption from the Kachua groundwater is shown in Fig. 6. Based on the results, a coal dose of 2g/L and a mixing time of 1h were employed in

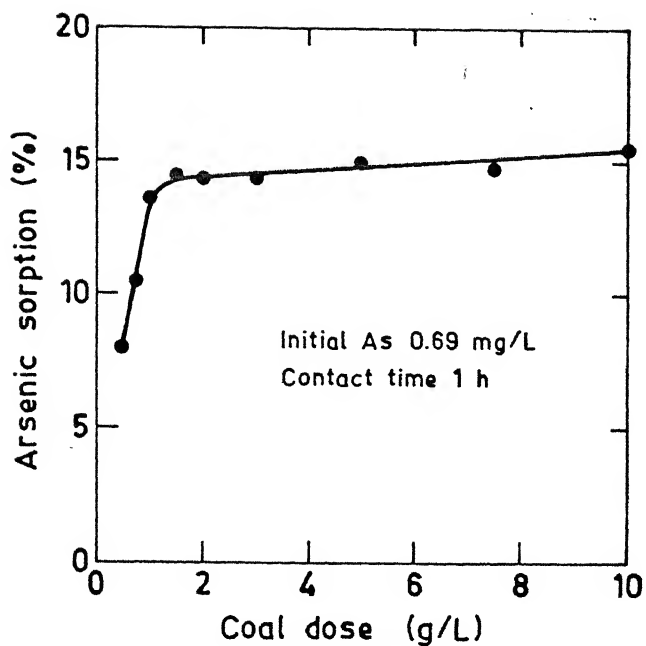


Fig. 6. Sorption of arsenic by powdered Giridih bituminous coal from Kachua groundwater.

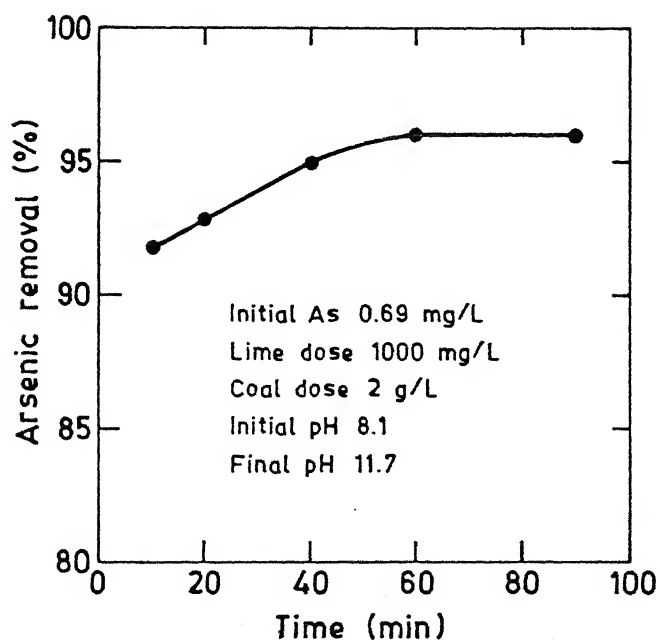


Fig. 7. Optimum mixing time for arsenic removal from Kachua groundwater by lime softening with powdered Giridih bituminous coal additive.

lime softening tests with powdered coal additive. This is further supported by the data presented in Fig. 7.

Arsenic removal from Kachua groundwater by lime softening with powdered Giridih bituminous coal additive is shown in Fig. 8. Residual arsenic level below the WHO guideline value (0.05 mg/L) can be achieved at a lime dose of 800 mg/L (pH 11.5) with 2g/L powdered coal. Powdered coal additive produced both enhancement of arsenic removal and reduction of lime dose. Comparison of data presented in Fig. 9 with those of Fig. 8 indicate that addition of coal and lime simultaneously or separately did not influence arsenic removal.

5.4 Role of Calcium Carbonate and Magnesium Hydroxide in Arsenic Removal

Sorption of arsenic(III) and arsenic(V) by preformed calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) precipitates was studied in order to ascertain the relative role of the two precipitates in removing arsenic by lime softening (Fig. 10 and 11). Evidently, $\text{Mg}(\text{OH})_2$ is more effective than CaCO_3 in terms of both arsenic(III) and arsenic(V) sorption, thereby indicating its more significant role in removing arsenic, particularly arsenic(III), by lime softening. The results also indicate that adsorption of arsenic by the precipitates is apparently more significant than coprecipitation in removal of arsenic. However, more detailed studies are needed to delineate the mechanism of arsenic removal by lime softening.

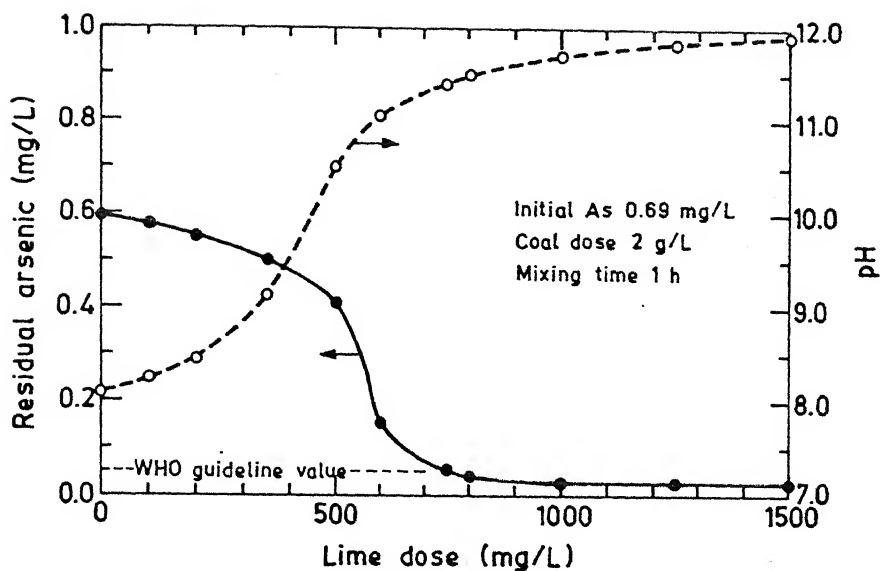


Fig. 8. Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater with powdered Giridih bituminous coal additive (coal and lime added simultaneously).

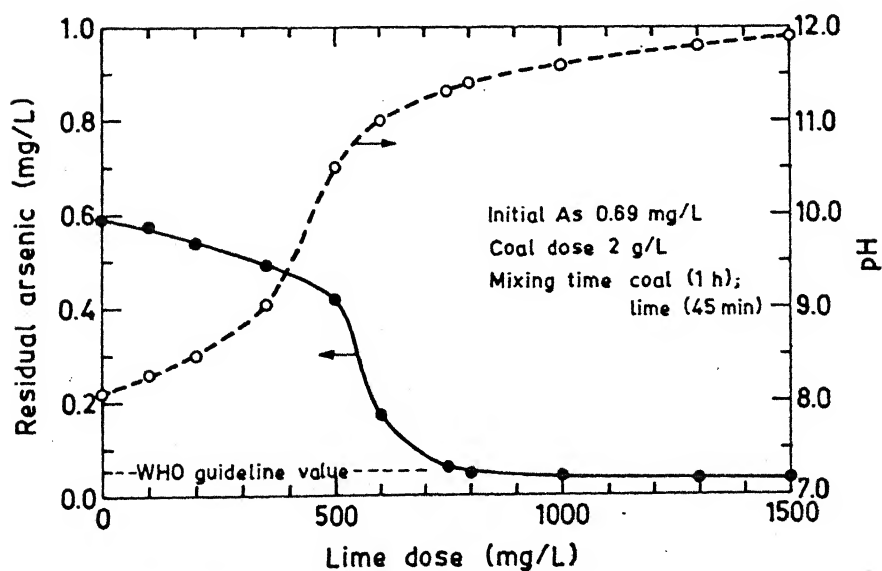


Fig. 9. Residual arsenic and pH vs. lime dose in lime softening of Kachua groundwater with powdered Giridih bituminous coal additive (coal and lime added separately).

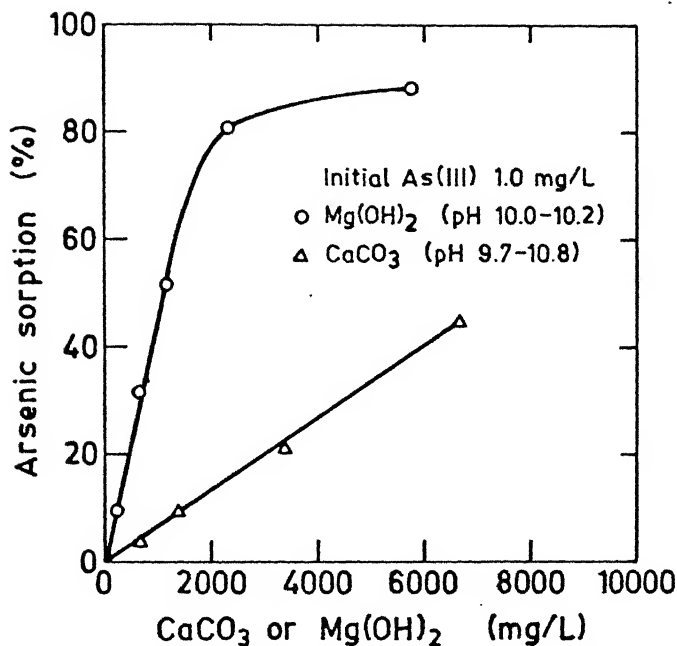


Fig. 10. Sorption of arsenic(III) by preformed calcium carbonate and magnesium hydroxide.

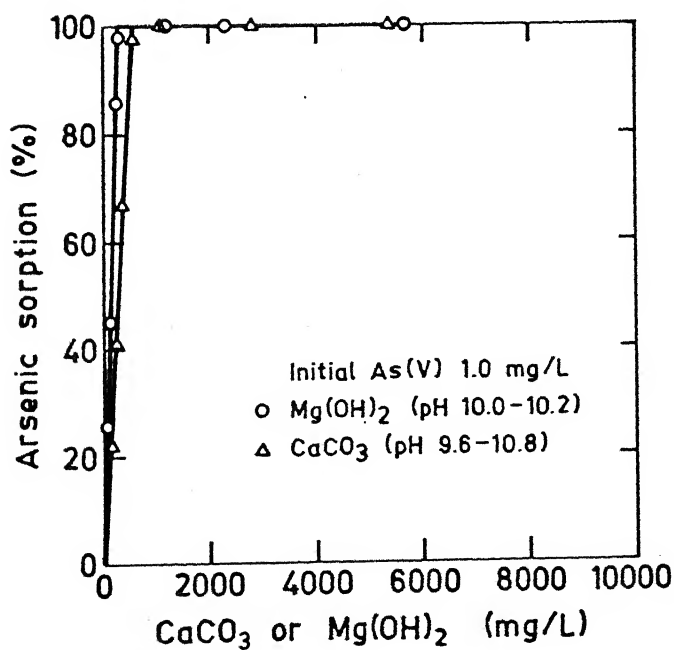


Fig. 11. Sorption of arsenic(V) by preformed calcium carbonate and magnesium hydroxide.

6. SUMMARY AND RECOMMENDATIONS

The present study stemmed from the reported high ground-water arsenic levels and associated health problems in some parts of West Bengal. Removal of arsenic by lime softening from tubewell water samples collected from one of the affected areas (Kachua village, 24 Parganas (N), West Bengal) was studied in the laboratory. The Kachua groundwater samples showed total arsenic concentration in the range 0.45-0.70 mg/L with 85.7-86.8% arsenic(III). A low-volume laboratory lime softening test procedure (75 mL groundwater; 45 min mixing in an end-over-end shaker at 20 rpm; filtration through Whatman No. 42 filter paper) was standardized using arsenic (III) (1.0 mg/L) spiked IIT Kanpur groundwater. Tests with the Kachua groundwater produced maximum arsenic removal of 89% (residual arsenic 0.07 mg/L) at a lime dose of 1250 mg/L (pH 11.80). Lime softening with powdered coal additive was investigated with a view to produce residual arsenic levels below the WHO guideline value for arsenic (0.05 mg/L). With 2 mg/L of powdered Giridih bituminous coal additive, it was possible to achieve a residual arsenic level below the WHO guideline value at a lime dose of 800 mg/L (pH 11.5). Addition of lime and powdered coal simultaneously (mixing time: 1h) or separately (mixing time: coal 1h; lime 45 min) produced comparable residual arsenic levels. Arsenic(III) and arsenic(V) sorption by preformed calcium carbonate and magnesium hydroxide precipitates indicated that magnesium hydroxide played a more significant

role in removing arsenic, particularly arsenic(III), by lime softening. More detailed studies are suggested to delineate the mechanism of arsenic removal by lime softening vis-a-vis the significant role of magnesium hydroxide in arsenic removal. This would facilitate proper design of lime softening units for low-magnesium arsenic-containing groundwater supplies.

It is recommended that a field-scale lime softening demonstration plant (with recarbonation facility) for arsenic removal be set up in one of the affected areas of West Bengal and monitored for its performance to evolve design and operation criteria.

REFERENCES

- Arguello, R.A., Cenget, D.D. and Tello, E.E. (1938). Cancer and Endemic Arsenism in the Cordoba Region. Rev. Argenl. Dermatositilogr, 22:461.
- Bellack, E. (1971). Arsenic Removal from Ground Water. J. Am. Water Works Assoc., 63:454.
- Berezman, R.I. (1956). Removal of Inorganic Arsenic from Drinking Water Under Field Conditions. Water Poll. Abstr., 29:185.
- Bhatla, M.N., Briedenbach, A.W. and Weston, R.F. (1980). Treatability of Priority Pollutants: Status Review and Case Studies. Water 1979, Am. Inst. of Chem. Engrs. Symp. Series, 76:25.
- Borgono, J.M. and Greiber, R. (1972). Epidemiological Study of Arsenicism in the City of Antofagasto. Proc. 5th Annual Conference on Trace Stustance in Environmental Health, University of Missouri, Columbia, Missouri.
- Buswell, A.M., Gore, R.C., Hudson, H.E., Wiese, H.C. and Larson, T.E. (1943). Water Problems in Analysis and Treatment. J. Am. Water Works Assoc., 35:1303.
- Chakraborty, A.K. and Saha, K.C. (1987). Arsenical Darmatosis from Tubewell Water in West Bengal. Indian J. Med. Research, 85:326.
- Chen, K.D. and Wu, H. (1962). Epidemiological Studies on Black-Foot Disease II: A Study of Source of Drinking Water in Relation to the Disease. J. Formosa Med. Assoc., 61:611.
- Cullen, G.V. and Siviour, G.N. (1982). Removing Metals from Waste Solutions with Low Rank Coals and Related Materials. Water Research, 16:1357.
- Curry, N.A. (1972). Philosophy and Methodology of Metallic Waste Treatment. Presented at 27th Purdue Industrial Waste Conference, Purdue Univ., West Lafayette, Indiana.
- Datta, D.V. and Kaul, M.K. (1976). Arsenic Content of Drinking Water in Villages in Northern India. J. Assoc. Physicians India, 24: 599.
- Ferguson, J.F. and Gavis, J.A. (1972). Review of Arsenic Cycles in Natural Waters. Water Research, 6:1259.

- Fox, K.R. (1989). Field Experience with Point-of-Use Treatment Systems for Arsenic Removal. J. Am. Water Works Assoc., 81:94.
- Goldblatt, E.L., Vandenburg, A.S. and Marsland, R.A. (1963). The Usual and Widespread Occurrence of Arsenic in Well Waters of Lane Country. Oregon Department of Health, Oregon.
- Guha, S. (1989). Removal of Arsenic(III) from Groundwater by Adsorption on Low-Cost Material. M.Tech. Thesis, Department of Civil Engineering, I.I.T., Kanpur.
- Gulledge, J.H. and O'Connor, J.T. (1973). Removal of Arsenic(V) from Water by Adsorption on Aluminium and Ferric Hydroxides. J. Am. Water Works Assoc., 65:548.
- Hathway, S.W. and Rubel, F. (1987). Removing Arsenic from Drinking Water, J. Am. Water Works Assoc., 79:61.
- Huang, C.P. and Fu, P.L.K. (1984). Treatment of As(V) Containing Water by Activated Carbon Process. J. Water Poll. Control. Fed., 56:233.
- Hurlbut, C.S. (1968). Minerals and Man. Random House, New York.
- Kuo, T. (1968). Arsenic Content of Artesian Wellwater in Endemic Area of Chronic Arsenic Poisoning. Rep. Inst. Pathol. (Natl. Taiwan Univ.), 20:7.
- Laguitton, D. (1976). Arsenic Removal from Gold-Mine Wastewaters: Basic Chemistry of the Lime Addition Method. Can. Inst. Metals Bull., 69:773.
- Logsdon, G.S., Sorg, T.J. and Symons, J.M. (1974). Removal of Heavy Metals by Conventional Treatment. Proc. 16th Water Quality Conference. Univ. of Illinois Bull., 71:111.
- Lyubman, N.Y., Bezera, S.V. and Kamulbaeva, M.S. (1981). Research of Arsenic(III) Precipitation by Calcium Hydroxide. Chem. Abstr., 94:335 (19).
- National Research Council, (1977). Drinking Water and Health. National Academy of Sciences, Washington, D.C.
- Patterson, J.W. (1975). Industrial Waste Treatment Technology. Ann Arbor Science Pub. Inc., Ann Arbor, Michigan.
- Quebec Ministry of Supply and Services. (1979). Guidelines for Canadian Drinking Water Quality 1978. Quebec, Canada.

- Rosehart, R. and Lee, J. (1972). Effective Methods of Arsenic Removal from Gold-Mine Wastes. Can. Min. J., 65:53.
- Rosenberg, H.G. (1973). Systemic Arterial Disease with Myocardial Infraction : Report on Two Infants. Circulation, 47:270.
- Sedova, V.A., Kogan, B.I. and Vishnyakova, N.N. (1974). Use of the Principle of Coprecipitation with Calcium Carbonate for Complete Removal of Arsenic from Waste-Water. Tsveln. Met., : 27.
- Shen, Y.S. (1973). Study of Arsenic Removal from Drinking Water. J. Am. Water Works Assoc., 65:543.
- Sorg, J.T. and Logsdon, G.S. (1978). Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics : Part 2. J. Am. Water Works Assoc., 70:379.
- Standard Methods for the Examination of Water and Wastewater (16th Ed.). (1985). American Public Health Association, Washington, D.C.
- Tereda, H. (1960). Clinical Observation of Chronic Toxicosis by Arsenic. Nihon Rinsho, 18:118.
- Train, R.E. (1979). Quality Criteria for Water. Castle House Pub. Ltd., Washington, D.C.
- Trelles, N. and Amato, F.D. (1950). Treatment of Arsenical Waters with Lime. Water Poll. Abstr., 23:125.
- Tseng, W., Chen, V., Sang, J. and Chan, J. (1961). Study of Black-Foot Disease in Twaiwan : An Epidemic of Peripheral Vascular Disease. Mem. College Med., 7:1
- Wenk, E. (1969). The Physical Resources of the Ocean. Scientific Am., 221:171.
- WHO (1981). Arsenic. Environmental Health Criteria 18. World Health Organization, Geneva.
- WHO (1984a). Guidelines for Drinking Water Quality. Vol. 1. Recommendations. World Health Organization, Geneva.

WHO (1984b). Guideline for Drinking Water Quality. Vol. 2. Health Criteria and Other Supporting Information. World Health Organization, Geneva.

Woodward, F.L. (1960). Significance of Pesticides in Water Supplies, J. Am. Water Works Assoc., 52:1367.